3

X-RAY ANALYSIS OF FROZEN PYRIDINE AND ITS SOLUTION AT −180°C

S. G. BISWAS

Optics Department, Indian Association for the Cultivation of Science, Jadavpur, Calcutta.

(*Received for publication, September 2, 1957*)

Plate II

ABSTRACT. Debye-Scherrer patterns of pure pyridine and its solution in the frozen state at −180°C have been studied and two different patterns due to crystals of pyridine have been observed. Analysis of the patterns show that the first modification belongs to the space group Q^1_h with $a=12.16$ A.U., $b=9.14$ A.U., $c=8.18$ A.U. and the second modification belongs to the space group Q^2_h with cell dimensions $a=11.00$ A.U., $b=9.27$ A.U., $c=9.02$ A.U. The density of the crystals has also been measured and the number of molecules in the unit cell is found to be 8 in both the cases.

It is pointed out that pyridine molecule is asymmetric in both the modifications and that the formation of weak bonds among the molecules in the solid state may be the cause of such asymmetry. The frozen mixture is found to be amorphous. These results are compared with those of the investigations on the Raman spectra of crystals of pyridine and of frozen mixtures of pyridine by previous workers and it is concluded that complex groups of molecules produced new Raman band in the frozen mixtures.

INTRODUCTION

The Debye-Scherrer patterns of toluene and its mixtures with alcohol in the solid state at −180°C were studied recently by Biswas and Sirkar (1957) and it was observed that frozen toluene belongs to the space group C_{2v}^7, and that certain frozen mixtures of toluene and alcohol which appear to form glass are amorphous. These results, combined with those of the investigations on the Raman spectra of these substances (Kastha, 1956a), throw some light of the nature of intermolecular forces present in these solid masses at −180°C.

It was further observed by Kastha (1956) that solid pyridine at −180°C produces new Raman lines in the low frequency region and that frozen mixtures of pyridine with alcohol produce a new Raman band instead of a few new lines given by pure pyridine in the solid state. It was not known, however, whether the mixtures of pyridine with alcohol in the solid state are crystalline and the crystal structure of pyridine was also not known. The present investigation was undertaken to study the Debye-Scherrer patterns of frozen pyridine and of its solutions in alcohol at −180°C in order to correlate the results with those observed in the investigations on the Raman spectra of these substances. It was also

intended to find the space group of the crystals of pure pyridine and to determine the symmetry of the molecule in the crystal.

EXPERIMENTAL

Pyridine used in the investigation was of chemically pure quality. Debye-Scherrer patterns of pyridine and of 50% solution of pyridine in dehydrated ethyl alcohol in the frozen state at - 180°C were photographed using a low-temperature camera of special design. The liquid was sealed in thin-walled glass tube which was fixed vertically along the axis of a cylindrical camera and was rotated slowly during the exposure by an electric motor and a gear system. A narrow stream of liquid oxygen was falling continuously through a funnel on the tube containing the liquid from a Dewar vessel of special design fitted on the lid of the cylindrical camera which was evacuated continuously with a pump. With this arrangement well-defined Debye-Scherrer rings were produced by frozen pyridine, but a halo due to liquid oxygen was superposed on the pattern. The radius of the camera was measured by photographing the Debye-Scherrer pattern due to rock salt.

A Seifert X-ray tube running at 32 KV and 26 mA was used to photograph the Debye-Scherrer patterns. The X-ray tube was provided with a copper target and a nickel filter was used to cut off the Kβ radiation. An exposure of $2\frac{1}{2}$ hours was sufficient to record each pattern with moderate intensity. Several photographs were taken in each case to confirm the genuineness of the results. It was observed, however, that in some of these photographs the pattern was similar to that due to a fibre, while in the other photographs uniform rings were obtained. So both these patterns were recorded carefully to find out whether they indicated different structures.

RESULTS AND DISCUSSION

The two types of pattern due to frozen pyridine at - 180°C are reproduced in figures 1 and 2, Plate II. The values of $\sin^2\theta$, calculated from these Debye-Scherrer photographs of frozen pyridine at - 180°C, are given in Tables I and II respectively. These values indicate that the structure is not the same in the two cases. By applying Lipson's method (Lipson, 1949) to the values of $\sin^2\theta$ the crystal system was found to be ortho-rhombic in both the cases. The values of $\lambda^2/4a^2$, $\lambda^2/4b^2$, and $\lambda^2/4c^2$ deduced from the values of $\sin^2\theta$ by Lipsons' method are given below :

(a) *Modification I* (figure 1) $\lambda^2/4a^2 = .00401$, $\lambda^2/4b^2 = .00710$

$$\lambda^2/4c^2 = .00825.$$

From these we get

$$a = 12.16 \text{ A.U}, \quad b = 9.14 \text{ A.U} \quad c = 8.48 \text{ A.U}.$$

To calculate the number of molecules per unit cell, the density of pyridine at $-180°C$ was required, but it was not found in the existing literature. So the density of frozen pyridine at $-180°C$ was measured in the same way as in the case of toluene (Biswas and Sirkar, 1957) and it was found to be 1·134. The number of molecules per unit cell calculated with this value of the density is approximately 8.

The values of $\sin^2\theta$, calculated with those of $\lambda^2/4a^2$, $\lambda^2/4b^2$ and $\lambda^2/4c^2$ mentioned above, the spacings and indices of the corresponding planes are, also included

TABLE I

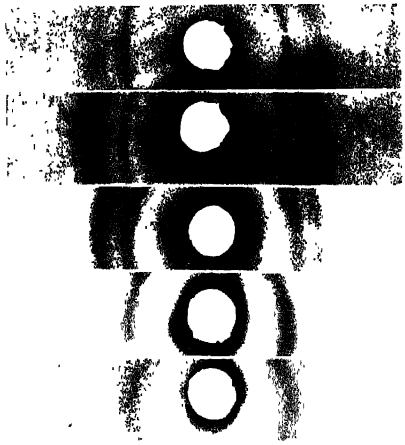
$\sin^2\theta$ (observed)	$\sin^2\theta$ (calculated)	Difference	Spacings in A U	Indices and Intensities
01650	01604	.00046	5·99	200 (m)
.02826	02840	00014	4·58	020 (m)
03287	03300	00013	4·25	002 (vs)
03735	03701	00034	3·98	102 (w)
04264	.04319	00055	3·73	310 (vw)
04857	04904	.00047	3·49	202 (s)
05319	05260	00050	3·34	221 (s)
07089	07126	00037	2·89	410 (s)
07939	07951	.00012	2·73	411 (s)
.09670	09716 .09690	00046 00020	2·47	402 (vw)* 032
11330	.11360	00030	2·29	040 (w)
13220	13200	00020	2·12	004 (w)
14940	14969	00029	1·99	340 (m)
.16230	.16264	.00034	1·91	242 (vw)
17680	.17644	.00036	1·83	224 (w)
19630	.19616	00014	1·71	104 (vw)

*br

TABLE II

$\sin^2\theta$ (observed)	$\sin^2\theta$ (calculated)	Difference	Spacings in A.U	Indices and Intensities
.02785	02760	00025	1 61	020 (s)
02966	02920	00046	1 47	002 (vs)
03384	03380	00004	1 19	211 (s)
.04100	.04120	00020	3.80	112 (vw)
04857	04880	00023	3 49	202 (s)
.05423	05450	00027	3 31	221 (m)
06947	06940	00007	2 92	031 (s)
07877	07840	00037	2 74	400 (s)
09656	09620	.00036	2 48	132 (m)
11070	11040	.00030	2 32	040 (m)
.13000	.13000	00000	2.13	240 (w)
13610	13640	00030	2 09	204 (vw)
14420	14440	.00020	2 03	024 (m)
14940	14930	.00010	1 99	124 (m)
15110	15100	.00010	1 98	413 (w)
15930	.15920	.00010	1 93	342 (w)
16810	16780	.00030	1 88	314 (vw)
17640	17640	.00000	1 83	600 (m)
19400	19430	.00030	1 75	115 (m)

in Table I. The intensities are indicated roughly by the letters "s, m, w" etc in parentheses It can be seen from Table I that there is no restriction for the occurrence of reflection from the planes. The ring due to (400) is masked by the liquid oxygen halo The want of restriction leads to the conclusion that the space group C_h^1 and as the number of molecules in the unit cell is eight, the molecule has no symmetry in the frozen state at - 180°C. So, there is neither a plane of symmetry nor a two-fold axis of symmetry in the molecule in this modification of the crystal This indicates that probably there is unusual bond-formation among the molecules in the solid state. This also supports the view put forward by Kastha (1956) that groups of pyridine molecules formed in the solid state produce new Raman lines in the low-frequency region.



X-ray photographs

Fig. 1 Pyridine (modification I) at −180°C
Fig 2 ,, (modification II) ,, ,,
Fig. 3 50% mixture at −180°C
Fig 4 50% ,, at 30°C
Fig 5 Pure pyridine at 30°C

(b) *Modification II.*

In this case the values of $\lambda^2/4a^2$, $\lambda^2/4b^2$ and $\lambda^2/4c^2$, which explain the observed values of $\sin^2\theta$ given in Table II satisfactorily, are .0049, .00690 and .00735 respectively. These give the following cell dimensions·

$$a = 11.00 \text{ A.U.}, \quad b = 9.27 \text{ A.U}, \quad c = 9.02 \text{ A.U.}$$

If the density is taken as 1.134 in this case also the number of molecules per unit cell comes out as 7.94. This shows that the number of molecules per unit cell is 8 in both the modifications and the differences between this value and those calculated in the two cases may be due to some uncertainty in the value of the density.

Table II shows that planes (221), (124) and (115) produce Debye-Scherrer rings in this case. These rings could not be assigned alternative indices. So there seems to be no restriction in this case also except that (okl) is halved if $(k+l)$ is odd, (hol) is halved if $(h+l)$ is odd and (hko) is halved if $(h+k)$ is odd. These restrictions and the number of molecules per unit cell indicate that the space group is Q_h^2 and the molecules are all asymmetric in this case also. It appears that rotation through a small angle of the molecules about the b-axis is responsbile for producing the second modification.

II. *Structure of frozen solutions of pyridine.*

The patterns due to a 50% solution of pyridine in ethyl alcohol both in the solid state at −180°C and at the room temperature and that due to pure pyridine in the liquid state are reproduced in figures 3, 4 and 5 (Plate II) respectively. Pure pyridine in the liquid state produces a broad halo giving a mean spacing of 4.65 A.U. The mixture in the liquid state produces a similar halo corresponding to a spacing of 4.43 A.U The frozen solution shows a single halo inside another halo due to liquid oxygen and the spacing is 4.17 A.U.

It was reported earlier (Biswas and Sirkar, 1957) that frozen ethyl alcohol produces ring corresponding to a spacing of 3 78 A.U. Hence the spacing observed in the case of mixture of pyridine in ethyl alcohol is just the mean of the spacings due to two pure liquids. This shows that the mixture is a homogeneous one. Further, the spacings observed in the frozen mixture of pyridine in ethyl alcohol is much larger than that in the frozen in cybotactic groups in solid ethyl alcohol This shows that in this mixture there are certain frozen-in cybotactic groups formed by interpenetrating pyridine and ethyl alcohol molecules. Evidently the new Raman band at 95 cm^{-1} observed by Kastha (1956) in the Raman spectrum of such a frozen mixture is produced by frozen-in groups of molecules in which both pyridine and alcohol molecules are present. Since the whole structure is amorphous, the intermolecular vibration, which gives rise to this band, must be confined to very small groups of molecules, each group containing both types of mole-

cules. The value of the frequency-shift indicates that the weak bond which holds the two types of molecules together in these smaller groups must be many times stronger than the Van der Waals forces expected to be present in the lattice. Hence, all these results indicate that formation of some weak bonds between pyridine and ethyl alcohol molecules takes place in the frozen mixture and very small groups oriented in the same way in small portion throughout the volume form frozen-in cybotactic groups in the amorphous mass

ACKNOWLEDGEMENT

The work has been carried out under a scheme financed by the Council of Scientific and Industrial Research and the author is indebted to the Council for the financial help The author is also indebted to Professor S C. Sirkar, D.Sc., F.N.I., for his kind interest and guidance during the progress of the work

REFERENCES

Biswas, S G. and Sirkar, S C., 1957, *Ind. J Phys.*, **31**.
Kastha, G S., 1956a, *Ind. J Phys.*, **30**, 313.
„ „ 1956, *Ind J. Phys.*, **30**, 519
Lipson, H., 1949, *Acta Cryst.*, **2**, 43.